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MICROBIOLOGICALLY INFLUENCED CORROSION OF DISPOSAL CONTAINERS FOR RADIOACTIVE WASTES

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ABSTRACT

Microbiologically influenced corrosion has been documented for all metals and alloys currently in use or proposed for packaging nuclear wastes, with the possible exception of titanium. Selection of a material that will provide a reliable physical barrier to prevent leakage of radionuclides will depend on a thorough understanding of mechanisms for microbiologically influenced corrosion, the geological/microbiological/chemical environments of storage sites and their evolution over time.

INTRODUCTION

Microbial biofilms develop on all surfaces in contact with aqueous environments. Biofilms composed of immobilized cells embedded in an organic polymer matrix are absorptive and porous, and contain solutes, heavy metals, and inorganic particles, in addition to cellular constituents (1). Biofilm/surface interfacial chemistry can be radically different from that of the bulk medium in terms of pH, dissolved oxygen, organic and inorganic species. Microbiologically influenced corrosion (MIC) is usually used to designate corrosion due to the presence and activities of microorganisms within biofilms at metal surfaces. It is important to extend the definition to include corrosive microbial metabolites that may be produced in one location and diffuse to a corrosion site. MIC is localized corrosion that results in pitting, selective leaching, crevice corrosion, under-deposit corrosion and enhanced erosion corrosion. Microorganisms can accelerate rates of partial reactions in corrosion processes and shift corrosion mechanisms.

MIC of storage containers is a potential problem for safe disposal of nuclear wastes. Primary materials being considered for containment of high level nuclear waste in mined geological repositories are alloys of iron, nickel, copper and titanium. Iron and nickel are significant components of alloys being proposed for containment of low- and intermediate-level nuclear waste in either shallow land burial or deep disposal. Aluminum and stainless steel alloys are currently used in the construction of pools and racks for storage of spent nuclear fuels. Carbon steels have been used to contain nuclear wastes in marine sediments (2) and are being considered as suitable materials for the outer shell of a double shell storage container for subsurface burial. With the

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exception of titanium, MIC has been documented for all metals and alloys under consideration. However, because of a lack of information about subsurface/oligotrophic microbiology and the belief that γ -radiation from fuel within containers would effectively sterilize storage environments, recognition of potential problems has been neglected. In this paper mechanisms and case histories for MIC will be reviewed with particular attention to metals and alloys currently in use or proposed for nuclear waste storage.

Biofilm Formation

Presence of water, availability of nutrients/energy sources and tolerance of microorganisms to high temperature, ionizing radiation and concentrated solutes will influence development of a substantial population of microorganisms on or around nuclear waste storage containers. There is increasing evidence that microorganisms exist and flourish in unlikely environments, including radioactive and nutrient-deficient waters and deep subsurface environments. Algae, fungi, yeasts and bacteria were found in water covering the damaged reactor core at Three Mile Island (TMI) nuclear power plant (3). Bacteria survived on carbon-rich hydraulic fluid leaked from tools during defueling after exposure to γ -radiation doses of 10 Gy h^{-1} (4). Dose rate around a nuclear waste storage container decreases with time as waste decays and decreases with increasing distance because of attenuation in buffer material.

Groundwaters in geological deposits are often saline and typically contain 10^1 to 10^5 colony-forming units ml^{-1} (5). Three significant biofilms containing bacteria have been identified at the Underground Research Laboratory (URL) in the Archean Lac du Bonnet Batholith in southeastern Manitoba: one at the drill hole draining through an underground structure (420 m depth), an extensive biofilm covering walls kept wet by groundwater flowing from fractures and exposed to gaseous carbon and nitrogen-containing explosives (240 m depth), and one found on the side of a large borehole (130 m depth) irrigated by water from drilling operations. The indigenous microbial population in the Canadian design disposal vault was relatively small (10^3 to 10^5 microbes cm^{-3}) compared with surface waters (6). However, Stroes-Gascoyne (7) concluded that construction activity will introduce both microorganisms and nutrients. White et al. (8) found biochemical evidence that bacterial populations equivalent to 10^7 bacteria gm^{-1} sediment existed at a depth of 410 m in the Bacatunn clay formation near Pensacola, FL. Viable microorganisms were recovered in Nevada from ashfall tuff in a mined tunnel 350-450 m below the surface and hundreds of meters above the regional water table. Microorganisms adhere to rock surfaces and form complex, sessile biofilm populations that intervene between rock and groundwater (9). In soils and on rock surfaces, microorganisms are generally not uniformly distributed but accumulate in discrete microcolonies attached to particle surfaces to form a system composed of more or less discontinuous colonies, each in its own microhabitat (10).

In natural oligotrophic environments the formation of biofilms is a survival strategy.

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for bacterial communities. Little et al. (11) reviewed factors influencing adhesion of microorganisms to substrata. Roughness and surface chemistry of the substratum play a major role in biofilm processes during early stages of biofilm accumulation and may influence rate of cell accumulation and distribution in aquatic environments. Electrolyte concentration, pH and inorganic ions influence settlement. Hydrated oxide and hydroxide passivating films on metal surfaces provide bacteria with sites for firm attachment. Similarly, spalling or sloughing of corrosion products forces detachment of biofilms associated with corrosion products. Carbon is not always the growth limiting nutrient for microorganisms. Phosphorus and nitrogen may be limiting in some systems. Wilkinson (12) found that, when the concentration of nitrogen in a growth medium was gradually lowered until it became limiting with C/N ratios in the range 7-10, cells growing in such a medium tended to reproduce slowly and produced copious amounts of extracellular polymer. Hydrodynamic shear stress, related to flow, influences transport, transfer and reaction rates within biofilms, as well as detachment. Temperature influences the rate of most chemical and biochemical reactions as well as transport processes within the biofilm.

In several proposed storage concepts, used nuclear fuel would be encapsulated in a metal container and buried in an underground disposal site located 500 to 1000 m subsurface. Containers would be surrounded by a compacted mixture of silica sand and sodium bentonite, known as buffer material. Safety is based on a series of barriers designed to prevent or delay toxic radionuclide species from coming into contact with man. The only absolute barrier in the system is the container. All other barriers are porous. Sodium bentonite is a cation-exchanging smectite clay mineral that swells upon contact with water. Mass transport through the buffer is expected to occur only by diffusion. Remaining void spaces will be air-filled, and entrapped oxygen will be the major source of oxidants. Depending upon specific disposal design, containers will be embedded in buffer material in either excavated rooms or boreholes filled with clay, crushed rock, and/or concrete. The next barrier in the system is 500 to 1000 m of granitic rock, clay, salt, limestone, iron ore, gypsum, bitumen, ash or soil.

Storage environments in geological repositories and their microflora will change with time. Initially, conditions will be hot and oxidizing as radioactive decay of fuel produces heat and γ -radiation. Initial storage environments will be radioactive, hot, dry and nutrient deficient. Combined effects of elevated temperature, γ -radiation and desiccation of the buffer material will severely limit the extent of microbial activity close to the container and might result in an abiotic zone 40 cm into the compacted buffer material (13). As fuel decays and trapped oxygen is consumed, conditions are expected to become cool and anoxic. As the container surface temperature decreases, the buffer material will become fully saturated with ground water. Length of the resaturation period could be several to several thousand years. Microbial transport and growth during resaturation will be limited because of spatial restrictions within the buffer material.

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(mean pore size 0.1 to 0.5 μm), absence of large amounts of unbound water and availability of nutrients.

MECHANISMS FOR MICROBIOLOGICALLY INFLUENCED CORROSION

Concentration Cells

The physical presence of microbial cell surfaces, in addition to their metabolic activities, modifies electrochemical processes. Adsorbed cells grow, reproduce and form colonies that are physical anomalies, resulting in local anodes and cathodes and formation of differential aeration cells. Under aerobic conditions, areas under respiring colonies become anodic and surrounding areas become cathodic. The anodic reaction will be metal dissolution and the cathodic reaction will be oxygen reduction. Mature biofilms prevent diffusion of oxygen to cathodic sites and diffusion of aggressive anions, such as chloride, to anodic sites. Outward diffusion of metabolites and corrosion products is also impeded. If areas within the biofilm become anaerobic, i.e., if the aerobic respiration rate within the biofilm is greater than the oxygen diffusion rate, cathodic reactions can include reduction of water molecules, hydrogen ions, hydrogen sulfides or hydrated metal ions.

Reactions Within Biofilms

It is traditional to discuss microorganisms within biofilms as aerobic or anaerobic and as individual species. However, microorganisms form synergistic communities that conduct combined processes that individual species cannot. Cell death or lysis within a well-developed biofilm does not necessarily mean a cessation of influence on electrochemical processes (14). Volatile corrosive gases such as hydrogen, hydrogen sulfide, carbon dioxide or ammonia produced by microorganisms might permeate porous backfill material and contact container surfaces.

Volcanic ash, granite, clay buffers, soil and seawater contain sulfate ions and sulfate-reducing bacteria (SRB) are common in those environments. Seawater contains 1 to 10 viable SRB ml^{-1} irrespective of depth or sample site. Marine bottom muds contain 10^2 to 10^5 viable cells gm^{-1} (15). SRB were found in approximately 25% URL ground water samples (16). SRB were isolated from British bentonite, suggesting that there were strains that could survive in the clay environment (17). In anaerobic, sulfate-containing media, SRB use sulfate ions as terminal electron acceptors, producing hydrogen sulfide that reacts with metals to form sulfide corrosion products. In addition, SRB can stimulate the cathodic reaction by removal of hydrogen.

When conditions around storage containers become wet, cool, and anoxic microbial activity is possible in the immediate vicinity of storage containers. It has not been established that individual cells will be able to traverse buffer materials to reach container surfaces and form a biofilm. If the abiotic zone is repopulated, SRB are expected to dominate the microflora and SRB-influenced corrosion might be possible

under the biofilm. However, the most aggressive corrosion of metals and alloys in the presence of SRB is observed when there are successive, alternating aeration-deaeration shifts. It is extremely unlikely that such shifts could occur under any disposal scenario. If repopulation of the abiotic zone cannot occur, SRB activity will be restricted to peripheral areas and impact on the container will result from diffusion of reduced sulphur species. King and Stroes-Gascoyne (18) demonstrated that inorganic sulfide will diffuse through a clay layer. It has not been demonstrated that sulfides produced by SRB will behave similarly. Most heterotrophic bacteria secrete organic acids during fermentation of organic substrates. The kinds and amounts of acids produced depend on the type of microorganisms and available substrate molecules. Organic acids may force a shift in the tendency for corrosion to occur. The impact of acidic metabolites is intensified when they are trapped at the biofilm/metal interface. Acetic acid from *Clostridium acetium* and sulfuric acid produced by sulfur-oxidizing bacteria (SOB), such as *Thiobacillus thiooxidans*, are obvious contributors to corrosion. Organic acids of the Krebs cycle can promote electrochemical oxidation of a variety of metals by removing or preventing the formation of an oxide film. Acid-producing fungal strains isolated from soil and autotrophic SOB degraded cement used as a coating material for low- and intermediate-level waste (19). Many organisms produce ammonia from the metabolism of amino acids or the reduction of nitrite or nitrate. In solution, ammonia forms NH_4^+ that can react with metal surfaces (20).

Metal-depositing organisms create environments that are conducive to corrosion. Some microorganisms catalyze the oxidation of metals, others accumulate abiotically-oxidized metal precipitates, and still others derive energy by oxidizing metals (21). Iron-oxidizing genera that are usually cited as causing MIC are *Gallionella*, *Sphaerotilus*, *Crenothrix* and *Leptothrix*. These organisms oxidize ferrous ions to ferric ions or manganous ions to manganic ions to obtain energy. Dense deposits of cells and metal ions create differential aeration cells that effectively exclude oxygen from the area immediately under the deposit. Under-deposit corrosion initiates a series of events that are individually and collectively extremely corrosive. In an oxygenated environment, the area immediately under the deposit becomes deprived of oxygen. That area becomes a relatively small anode compared to the large surrounding oxygenated cathode. Cathodic reduction of oxygen may result in an increase in pH of the solution in the vicinity of the metal. The metal will form metal cations at anodic sites. If the metal hydroxide is the thermodynamically stable phase in solution, metal ions will be hydrolyzed by water with formation of H^+ ions. If cathodic and anodic sites are separated from one another, the pH at the anode will decrease. The pH at the anode depends on specific hydrolysis reactions. The largest pH decreases are observed for alloys containing Cr^{+3} and Mo^{+3} . For this reason, under-deposit attack due to metal-depositing bacteria is particularly aggressive on stainless steels. In addition, Cl^- ions from the electrolyte will migrate to the anode to neutralize any buildup of charge, forming heavy metal chlorides that are extremely corrosive. Under these circumstances,

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pitting involves the conventional features of differential aeration, a large cathodic to anodic surface area ratio and development of acidity and metallic chlorides.

Walch and Mitchell (22) proposed the following roles for microorganisms in hydrogen embrittlement of metals: 1) production of molecular hydrogen during fermentation, which may be dissociated into atomic hydrogen and absorbed into metals, 2) production of hydrogen ions via organic or mineral acids which may be reduced to form hydrogen atoms at cathodic sites, 3) production of hydrogen sulfide which stimulates absorption of atomic hydrogen into metals by preventing its recombination into hydrogen molecules, and 4) destabilization of metal oxide films.

Microorganisms produce polymers and form gel matrices of bacterial exopolymers central to the structural integrity of microbial films. Polymeric gels can immobilize water, trap metal species/corrosion products and decrease diffusion. In general, exopolymers are acidic and contain functional groups that concentrate metal ions to form metal concentration cells. Geesey et al. (23) developed conceptual models for the acceleration of copper corrosion as a result of Cu^{+2} bound within exopolymers.

CASE HISTORIES

Ferrous Alloys

Eidsa and Risberg (24) and Sanders and Hamilton (25) analyzed microbial corrosion of carbon steels in North Sea oil exploration. SRB, SOB, hydrocarbon-oxidizing bacteria, iron-oxidizing bacteria, slime-forming bacteria and fungi were identified as causing corrosion. The following forms of SRB-mediated corrosion were defined: pitting caused by SRB growing in the biofilm on metal surfaces, sulfide-induced stress corrosion cracking (SCC), hydrogen-induced cracking, and blistering caused by hydrogen permeation in high dissolved sulfide conditions.

Marsh et al. (2) assessed the feasibility of disposing of heat-generating nuclear waste in deep ocean sediments in carbon steel containers that would not be breached for 1000 years. They concluded the following: 1) the main threat to long term integrity of containers was the external environment, 2) carbon steel would not be vulnerable to localized corrosion under disposal conditions, and 3) any corrosion threat could be accommodated by making container walls sufficiently thick. The authors did not consider MIC and the specific presence of SRB in marine sediments in their predictions. Carbon steel has also been considered as a container for geological disposal (26). These authors considered three types of corrosion: corrosion by oxygen, corrosion by reduction of water, and MIC. During 1000 years service life the contribution of SRB to localized corrosion was estimated to be 1.8 mm. Overall wall thickness required to accommodate the three types of corrosion was estimated at 300 mm.

Corrosion resistance of stainless steels is due to the formation of a thin passive film.

Passivity can break down under the following, usually localized, environments:

1. Dilute and concentrated HCl, HBr and HF and salts that hydrolyze these acids,
2. Oxidizing chlorides such as FeCl_3 , CuCl_2 or NaOCl ,
3. Seawater, except for brief exposures or when cathodically protected,
4. Some organic acids including oxalic, lactic and formic acids.

Microorganisms can produce the organic acids listed above. In addition, they can set up conditions for the formation of HCl and heavy metal chlorides. A persistent problem with the use of stainless steels is their susceptibility to crevice corrosion. Kobrin (27) identified iron- and manganese-oxidizing bacteria with localized corrosion of 304 and 304L stainless steels almost exclusively at weld seams. Pope (28) and Soracco et al. (29) described several cases of MIC in fossil fuel and nuclear power generating plants. Similarly, Puckorius (30) described the sudden failure of 304 stainless steel condenser tubes at an electric utility. There are no documented corrosion failures that can be attributed to MIC for the super stainless steels containing 6% molybdenum or more.

Sridhar and Cragnolino (31) evaluated localized corrosion of 316L stainless steel for possible storage of high-level nuclear waste materials in geological deposits without any specific reference to MIC. However, there are numerous reports of pitting and crevice corrosion due to MIC for this alloy exposed to sea, lake and service waters (11). Localized corrosion may be an important failure mechanism due to the propensity for under-deposit corrosion. Miller et al. (32) exposed 304L stainless steel samples in both vertical and horizontal planes to an inoculum of microorganisms from the TMI reaction vessel. Welded and non-welded vertical specimens showed no damage for twelve months. After twelve months, however, samples placed in a horizontal plane showed signs of corrosion at the weld.

Copper Alloys

Copper alloys are vulnerable to the following types of MIC: differential aeration cells, selective leaching, under-deposit corrosion and cathodic depolarization. Pope (28) proposed that the following microbial products accelerate localized attack: CO_2 , H_2S , NH_3 , organic and inorganic acids; metabolites that act as depolarizers; and sulfur compounds such as mercaptans, sulfides and disulfides. Pure copper and high-copper alloys are susceptible to SCC in ammonia-containing environments and in solutions containing nitrite or cupric acetate. Such environments might form within biofilms. Geesey et al. (23) demonstrated that extracellular polymers produced by bacteria play a role in corrosion of copper.

The impact of sulfides on corrosion of copper alloys has received considerable attention. In soils, sulfides increased the corrosion current of brass by a factor of 40 (33). Alloy 90/10 Cu/Ni suffered accelerated corrosion attack in seawater containing

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0.01 ppm sulfide after 1-day exposure (34). In the presence of waterborne sulfides, copper alloys form a porous layer of cuprous sulfide. Copper ions migrate through the layer, react with more sulfide, and produce a thick, black scale. Even if such a sulfide film were technically passivating, the film's mechanical stability is so poor that sulfide films are useless for corrosion protection. In the presence of turbulence, the loosely adherent sulfide film is removed, exposing a fresh copper surface to react with sulfide ions. For these reasons turbulence-induced corrosion and sulfide attack of copper alloys cannot easily be decoupled. In the presence of oxygen, the possible corrosion reactions in a copper sulfide system are extremely complex because of the large number of stable copper sulfides, their differing electrical conductivities, and catalytic effects. Transformations between sulfides, or conversions of sulfides to oxides, result in changes in volume that weaken the attachment scale and oxide subscale, leading to spalling (35). Bared areas repassivate, forming cuprous oxide. Neither circumstance is relevant for copper nuclear waste containers. Once anoxic conditions have been established within the disposal vault, they should remain anoxic indefinitely and there should be no mechanical disruption of intact sulfide layers should they form.

Copper canisters with 100 mm thick walls are being considered for final disposal of waste material from nuclear reactors by Swedish companies building nuclear power installations. Canisters would be placed in igneous rock 500 m below ground level. Copper plates that have been buried in three separate locations for more than 50 years as earth electrodes for lightning conductors were studied to determine the geochemical/microbiological properties of the ambient soil. Microbial activity was very low in comparison to that found in marine and brackish water sediments. Predominance of sulfides in the corrosion products did not correlate with redox potentials measured at the time of collection. Similarly, sulfide in corrosion products did not correlate with sulfate concentrations in soils. The pitting factor for two of the samples was five while the third sample was not pitted. Pitting factor is the ratio between maximum pit depth of a certain area and the mean depth of general corrosion in the same area (36).

Nickel Alloys

Commercially pure nickel and its alloys are susceptible to acid production at metal/biofilm interfaces and dealloying due to reactions with sulfide. Passivity of nickel is due to the formation of an oxide or hydrated oxide film several nanometers thick. Formation of protective films on nickel is aided by the presence of iron, aluminum and silicon. Passive films similar in structure to that observed on pure nickel are formed on Ni/Cu alloys having more than 30% nickel. Alloys containing less than this amount of nickel behave like copper. In high velocity seawater, nickel alloys are superior to predominantly copper alloys because the protective surface film remains intact under highly turbulent and erosive conditions.

Nickel alloys are susceptible to pitting and crevice corrosion attack under stagnant

conditions. Monel has a marked tendency for the initiation of pitting in chloride-containing environments where the passive film can be disturbed. Under stagnant conditions chlorides penetrate the passive film at weak points and cause pitting attack. Sulfides can cause either a modification of the oxide layer as described for copper or breakdown of the oxide film of nickel alloys. Brennenstuhl et al. (37) indicated that pitting of 3 nickel alloys containing 21-27% chromium exposed to untreated freshwater from Lake Ontario involved biofilm formation.

Aluminum and Aluminum Alloys

The corrosion resistance of aluminum and its alloys is due to an aluminum oxide passive film that is 20 to 100 Å thick for air-formed films. Anodizing produces thicker insulating films and better corrosion resistance. The susceptibility of aluminum and its alloys to localized corrosion makes it particularly vulnerable to MIC. After 12 months both Al 1100 (commercially pure aluminum) and Boral (a composite with a layer of boron carbide dispersed in aluminum and sandwiched between two sheets of Al 1100) showed pitting with accumulation of corrosion products in and over pits after exposure to organisms isolated from the TMI reactor vessel (32). Al 1100 also showed signs of crevice corrosion due to MIC. Kalaiyappan et al. (38) demonstrated MIC of Al 1100 and Al 6061 after a few weeks exposure to deionized water in a storage basin.

Titanium and Titanium Alloys

There are no documented case histories of MIC of titanium and its alloys. Schutz (39) reviewed titanium's resistance to MIC by discussing mechanisms for MIC and titanium's corrosion behavior. He concluded that at temperatures below 100°C titanium is not vulnerable to SOB, SRB, acid-producing bacteria, differential aeration cells, chloride concentration cells or hydrogen embrittlement. Formation of occluded regions of low pH underneath a biofilm could conceivably initiate crevice corrosion in titanium alloys (18).

CONCLUSIONS

Materials being considered for containment of nuclear waste in mined geological repositories are alloys of iron, nickel, copper and titanium. With the exception of titanium, MIC has been documented for all metals and alloys under consideration. The likelihood that MIC of nuclear waste storage materials will occur is directly related to the geological/microbiological/chemical environment of the storage site and vulnerability of the container material. Combined effects of elevated temperature, radiation and desiccation of buffer materials will severely limit the extent of microbial activity close to the container and might result in an abiotic zone into the compacted buffer material. If the abiotic zone is repopulated, SRB are expected to dominate the microflora and SRB-influenced corrosion might be possible for copper and nickel alloys and carbon steels.

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